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"UNIVERSAL" AIR POLLUTANT ANALYZER

D. F. Adams, et al

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

4 September 1957

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"UNIVERSAL" AIR POLLUTANT ANALYZER
(U.S.P.H.S. CONTRACT No.66512)

Prepared for

Community Air Pollution Program
Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

By

Institute of Technology
State College of Washington
Pullman, Washington

D. F. Adams, H. J. Dana and R. K. Koppe

September 4, 1957

U.S. Department of Health, Education, and Welfare
Public Health Service
Bureau of State Services
Division of Sanitary Engineering Services
Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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FOREWORD

The Air Pollution Research and Federal Assistance Act of 1955 (Public Law 159, 84th Congress) authorized the Public Health Service, U. S. Department of Health, Education, and Welfare, to carry on a program of research and technical assistance related to air pollution. As a means of expediting the air pollution research effort under this Program, the Act provides for the letting of research contracts. Contract research, as well as grant research, complements the activities carried on directly by the Public Health Service and by other Federal agencies.

One problem of air monitoring is the enormous range of concentrations in which pollutants may occur. Direct recording over such a range is most difficult; however, the single variable which can readily be recorded over the greatest dynamic range is time. For this reason, a contract was initiated with the Division of Industrial Research, Institute of Technology, State College of Washington, to study the feasibility of measuring levels of air pollutants in terms of the time required for a standard change to take place in liquid reagents.

The report of the work conducted under this contract, contained herein, is published and made available for the information of individuals and organizations to whom it will be useful.

STATE COLLEGE OF WASHINGTON PULLMAN, WASHINGTON

WASHINGTON STATE INSTITUTE OF TECHNOLOGY
DIVISION OF INDUSTRIAL RESEARCH

September 4, 1957

Mr. Arthur C. Stern, Chief
Community Air Pollution Program
Robert A. Taft Sanitary Engineering Center
4676 Columbia Parkway
Cincinnati 26, Ohio

Dear Mr. Stern:

Enclosed you will find two copies of the final report of the first year's development of a versatile dosimeter and/or recorder for use in the analysis of sulfur dioxide and hydrogen fluoride. One copy of this report has been sent directly to your Washington, D.C. headquarters and the Surgeon General for immediate appraisal of patentable possibilities in the instrument and reagents.

Your attention is specially directed toward the section, "Problems Requiring Further Investigation." Completion of these studies will greatly increase the practical worth of our development.

Very truly yours,

Donald F. Adams, Head
Air Pollution Research

DFA/aw

Encl.

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U.S.P.H.S. CONTRACT #66512 "UNIVERSAL AIR POLLUTANT ANALYZER"

Donald F. Adams, Robert K. Koppe
and Homer J. Dana

SUMMARY

Two prototype automatic atmospheric pollutant analyzers suitable for producing dosimeter or continuously integrated records have been designed and constructed. The Zirconium-Eriochrome Cyanine R reagent for fluoride and the Starch-Iodine Blue reagent for sulfur dioxide have been modified for use in the analyzers. The reduced stability of these reagents under continuous air aeration for periods exceeding 4-12 hours limits the pollutant concentration which may be accumulated by a single reagent charge. This appears, however, to be desirable from the viewpoint of field application. The instrument has been field-tested for three weeks in the vicinity of Mead, Washington and Waneta, British Columbia. Simultaneous comparisons were made between the Thomas Autometer, Titrilog and the Dosimeter for sulfur dioxide and an automatic scrubbing solution collector and the Dosimeter for hydrogen fluoride. The instrument shows greater sensitivity to these two pollutants than other instrumental methods commercially available.

INTRODUCTION

The problems involved in sampling air pollutants are often complex. Variables such as meteorological conditions, topography, rates of pollutant emission, gas phase chemical reactions at low concentrations in the atmosphere with or without ultraviolet radiation, etc., make it desirable to use automatic sampling and measuring devices wherever possible for the determination of the ever-changing pollutant levels in the atmosphere. Many instruments for the analysis of gaseous pollutants have been developed because of this need.

Sulfur dioxide was one of the first pollutants for which instrumentation was developed. Thomas and co-workers (21, 22, 23) based their "Autometer" upon a measurement of the change in electrolytic conductivity of a dilute sulfuric acid-hydrogen peroxide solution in which absorbed sulfur dioxide was oxidized to the sulfate ion. These workers have also adapted the "Autometer" for continuous analysis of carbon dioxide in the atmosphere (24). The commercial version of this analyzer may be purchased from Leeds and Northrup Company, Philadelphia (15).

The "Titrilog" (26) absorbs sulfur dioxide in an acidic bromide solution in which a constant low level of bromine is electrolytically generated. Absorbed compounds which are oxidized by bromine are titrated to a potentiometric endpoint. The resulting reduction in bromine level is sensed by an appropriate electrode system and additional bromine is then generated to maintain the original bromine concentration. The current required to generate this additional bromine is a measure of the sulfur dioxide present in the atmosphere. The "Titrilog" is available from the Consolidated Electrodynamics Corporation, Pasadena, California, (10).

Katz (13) described another method for the automatic determination of sulfur dioxide in the atmosphere involving a photometric measurement of the fading of the blue color of a starch-iodine solution in the presence of the reducing gas. This procedure has not been commercially developed.

None of these instruments are specific for sulfur dioxide. The "Autometer" will also record soluble, ionizable gases in the sampled air stream. The "Titrilog" measures other reducing gases such as hydrogen sulfide, mercaptans and unsaturated hydrocarbons. The starch-iodine method is less subject to interference from hydrogen sulfide than the "Titrilog" since neutral iodine is less reactive than bromine (22).

The Rubicon Company of Philadelphia has developed a continuous analyzer for hydrogen sulfide employing reflectance measurements from the lead acetate impregnated tape (20).

A laboratory model of a continuous analyzer for hydrogen fluoride has been described by Chaikin *et al*. (8). The method is based on the selective quenching of the fluorescence of

magnesium oxinate by fluoride ion (11). The contaminated air is drawn past the fluorescent compound previously impregnated on a filter tape. Changes in fluorescence are measured photometrically. Adams et al. (5) presented a preliminary description of an instrument suitable for the automatic determination of sulfur dioxide and hydrogen fluoride in the atmosphere. These instruments are not commercially available.

Oxidant recorders have been developed which measure, either colorimetrically or electrometrically, the amount of iodine liberated from buffered potassium iodide solutions (9, 17). The colorimetric instrument is available from Beckman Instruments, Inc., Fullerton, California (7). Oxidant levels have also been determined colorimetrically through the oxidation of phenolphthalein solutions (12).

The Austin Dual Recording Colorimeter (6) for oxidants embodies two colorimeters, one to measure color changes in a phenolphthalein reagent and the other to measure a ferrous thiocyanate reagent. Air is sampled at a fixed rate through a measured volume of reagent for a set sampling period. Readings of the transmittance of the reagents are automatically made and recorded before and after each sampling period.

Thomas et al. (25) recently described the application of a modified Greiz-Saltzman reagent for the automatic analysis of oxides of nitrogen in the atmosphere. Harold Kruger Instruments, San Gabriel, California (14) have marketed an analyzer which permits colorimetric analysis of the atmosphere for oxides of nitrogen and oxidant and conductivity measurements of sulfur dioxide levels in a single instrument. Separate gas flow panels are available for each pollutant and may be mounted within a single metal enclosure. Recordings are made on a multi-channel recorder. A monetary saving over buying three separate instruments for the three pollutants is claimed.

From the foregoing brief descriptions, it is obvious that the constructional details of most of the commercial and laboratory instruments embodying the described analytical methods virtually preclude simple conversion of a given instrument to the analysis of a pollutant other than the one for which it was designed. For most applications it would be necessary to obtain a different instrument for each pollutant to be determined. In addition, nearly all instruments include an expensive, continuous electronic-type potentiometric recorder. The records usually obtained from continuously recording instruments include a large percentage of recorder chart paper record indicating no pollution. Thus, great lengths of chart paper must be inspected in order to discover short term periods of significant pollution.

The extent of records obtained could be greatly reduced through application of the dosimeter principle of sampling. This method considers the varying time span necessary to accumulate equivalent pollutant concentrations. The pollutant being measured is continuously accumulated and retained until a pre-determined level

of pollutant is reached. The varying intensities of exposure to the pollutant at each sampling site are related on a time basis, the minutes, hours, or days required to accumulate equal pollutant concentrations represent equivalent exposure doses. Ideally, periods of several days with no pollution present would produce a single line entry from a simple time stamp. Practically, problems involving the stability of continuously aerated reagents appears to limit the maximum cycling time for each volume of reagent. Inherent in the dosimeter method of sampling is the possibility of utilizing reagent systems less sensitive to the pollutant being measured, but which are also much less responsive to diverse pollutants.

The initial monetary investment required to equip several sampling sites within an area of atmospheric pollution with a battery of instruments capable of producing continuous information for several pollutants may be prohibitive in many instances. Instrumentation investments by air pollution study groups could be reduced many fold if an automatic sampling and analysis system could be devised which would permit (1) simple conversion of the basic instrument from the analysis of one pollutant to another and (2) maintenance of a record in an inexpensive, yet significant manner.

Based on these considerations, a dosimeter-type instrument has been developed which is potentially capable of the analysis of any pollutant for which a colorimetric procedure exists or could be devised. It is belived that the instrument herein described could be produced at a reasonable price, would yield significant data concerning changing levels of atmospheric pollution, and will find wide application in the study of a variety of gaseous pollutants.

The prototype which has been constructed, however, embodies both dosimeter and continuous recording features. Continuous recording was desirable during the reagent development period to enable instantaneous observations of the reaction of the reagent in the analyzer under varying operational conditions. Operating models could easily be constructed in either the dosimeter or continuous recording manner, depending upon the requirements of the particular study.

The contracting agency stipulated that a dosimeter-type analyzer and reagents for the determination of atmospheric sulfur dioxide and hydrogen fluoride be developed. Within the framework of this contract a two-channel instrument was designed and built which permits simultaneous determination of these two pollutants. The constructional features are such that the instrument may have a potential application in the study of any pollutant for which a photometric procedure may be adapted.

DESCRIPTION OF EQUIPMENT

Two separate analyzer units were constructed and assembled within a single metal enclosure to permit simultaneous development

and field testing of reagents for the determination of sulfur dioxide and hydrogen fluoride in the atmosphere. Each analyzer consists of two fundamental components: (1) a colorimeter capable of either triggering a time stamp upon development of a preselected photocell output equivalent to some concentration of the pollutant which has been absorbed in the reagent (dosimeter model) or driving a recorder (the continuous recording model) and (2) an air-reagent contacting system in which a continuously circulating volume of reagent contacts a sampled air stream until a preselected concentration of the desired pollutant has been absorbed by the reagent. The additional equipment making up the analyzer permits these fundamental components to carry on their function in an automatic manner. The complete schematic flow diagram of this versatile analyzer is shown in Figure 1. The assembled analyzer is pictured in Figures 2 and 3.

One of the photometric systems consists of a Photovolt Model 501-M fluorescence photometer. This unit was slightly modified to permit continuous flow measurements. In addition, a removable 45^{o} mirror was installed to enable absorbance measurements in the ultraviolet and visible light ranges. This photometer also includes four ranges of amplification to permit increased sensitivity when required. A wide choice of analytical methods is afforded because of the versatility of this modified photometer.

The second analyzer utilizes a Photovolt Model 400-S continuous flow photometer. Without extensive modifications this instrument is limited to measurements of visible light absorbance. Its use, however, greatly reduced constructional costs and would undoubtedly be adequate for many applications.

A Hanovia S-4 mercury vapor light, connected to the power source through a Sola constant voltage transformer, is used as the light source with the Model 501-M photometer. A G.E. germicidal lamp, mounted in an interchangeable housing, may be easily substituted for the S-4 lamp when conducting measurements requiring short ultraviolet radiation of 2567A.

A 50 watt projection lamp, connected to the power source through a Sola constant voltage transformer, provides the light source for the Model 400-S photometer. Although it has been reported that these lamps have a relatively short life, this type of lamp has given uninterrupted service for periods exceeding six months under the existing operating conditions.

Both photometers are constructed to permit easy interchange of optical filters, thus providing a selection of wave bands of light suitable for use with the analytical reagents utilized. The Model 501-M also provides for insertion of a secondary light filter to block scattered ultraviolet light when the unit is operating as a fluorometer.

For dosimetry, the output voltage of the colorimeter is utilized to operate a time stamp by changing the grid voltage on a sharp cut-off triode normally biased beyond cut-off. A double

throw switch permits the time stamp to be operated when the photometer output reaches either a pre-determined maximum or minimum (Figure 4). This arrangement produced a tape record consisting of a line entry of the minute, hour, day and year at which each preselected dosimeter concentration of the desired pollutant was attained. Subtraction of each preceding time record from its following record provides the actual air sampling time involved in each dosimeter cycle.

In the continuously recording version, the output from each photometer is hooked across a separate voltage divider to provide a 50 mv. full scale signal to the Leeds and Northrup 0-50 mv. X_1X_2 recorder. This recorder utilizes two independently variable potentiometric measuring circuits. Two independent pens continuously record the output from each photometer when the analyzer is operating as a continuous recorder. The recorder circuit should be balanced against the standard reference cell at least once every two days under continuous operation.

A con-current type of air-reagent contacting system was selected to facilitate continual circulation of a small batch of reagent through an optical flow cell with a minimum of auxilary equipment. A detailed drawing of a typical contactor system is shown in Figure 5.

The sampled air stream is drawn through a rotometer mounted on the face of the analyzer. The air volume is regulated by means of a built-in air leak on the vacuum side of the Fisher air pump (P_1). Air entering under suction lifts the reagent, which has fallen by gravity through the optical path, up through the contacting column. The scrubbed air is passed out through the exhaust tube at the top of the system to the suction pump and the reagent drains back through the optical path. A constant head of reagent is maintained within the optical cell by means of the capillary tip at the lower end of the cell.

Existing pollutant analyzers do not continuously cycle a small reagent volume and continually sense the spectral character of the reagent as is required in the operation of a dosimeter-type instrument. Obviously, continual changes in humidity of the sampled air stream and the rate of air sampling will produce a continued and variable reduction in reagent volume through evaporation. Such volume changes would be sensed as increased light absorbance readings by the photometer. Therefore, an electronic liquid level control system (2) was designed to sense slight decreases in reagent volume within the air-reagent system and to maintain the reagent at its initial volume by injection of make-up water as required. Figure 5 also indicates the location of the liquid level sensing electrodes. The control system circuitry is shown in Figure 6. The introduction of small increments of make-up water is controlled by a Beckman "Titrimeter" valve (V_6).

Experience with the sulfur dioxide reagent indicated that the starch-iodine blue color is extremely temperature sensitive.

As the temperature in the analyzer cabinet rises, the color becomes bleached. Conversely, as the temperature decreases the color becomes darker. To minimize this temperature sensitivity, a 1/3 h.p. refrigerative compressor, thermoregulator, heat exchanger coils and blower were installed in the analyzer cabinet to maintain the interior cabinet temperature at 75°F. One inch thick Styrofoam sheet was used to insulate the cabinet walls.

A motor-operated, 2-minute, single cycle, multiple cam timer switch controls the sequencing of the various automatic operations of the analyzer during the reagent changing cycle. Table I indicates the timing of a typical reagent cycling operation.

TABLE I

SAMPLE CHANGING SEQUENCE

Time (Seconds)	Operation
0	recorder shut off
0	air pump turns off
0	dump valve opens
30	dump valve closes
30	rinse water turns on
35	rinse water turns off
35	air pump turns on
40	air pump turns off
40	dump valve opens
70	dump valve closes
70	reagent syringe pump turns on
100	reagent injection completed
100	air pump turns on
120	recorder turns on

The reagent changing cycle begins as the multi-cam timers shut off the air pump (P_1, Figure 1) and interrupt the photometer output to the recorder. A Leeds and Northrup "dump" valve #102-1-0-8, Std. 3358-M-EN-L (V_1) located at the lowest point in the air-reagent system permits the spent reagent to drain to waste. This valve then closes and solenoid valve (V_2) opens momentarily, introducing a small volume of rinse water. The air pump is energized momentarily, circulating the rinse water throughout the system. Valve V_1 again opens and later closes permitting the rinse water to drain to waste. The reagent injection syringe pump (P_2) then introduced 25 ml. of the reagent into the system. Electro-hosecock V_3 opens during the time required for the syringe to inject the reagent into the system. This valve prevents reagent from being drawn into the air contacting system during the air sampling cycle. The air pump then turns on; the recorder circuit closes; reset time delay relay resets, and the pawl drops into the cam notch on the multi-cam timer. This latter operation prevents the multi-cam timer from further cycling until the cams become reactivated either upon the attainment of a dosimeter concentration, conclusion of a pre-selected time, or a push of a reset button on the face of the analyzer.

Reagent is introduced into the air contacting system by means of a motor-driven syringe pump (P_2). A set of glass check valves (V_4) between the reagent storage bottle and the syringe pump prevents the reagent from being forced back into storage during the exhaust stroke of the syringe. In subsequent models the reagent volume will be introduced through a carefully timed solenoid valve from a constant head storage bottle. This arrangement will also eliminate the check valves (V_4) and simplify the construction. The reagent storage and water make-up bottles are protected with appropriate air traps. The traps may contain soda lime, activated charcoal, silica gel, alkaline pyrogallol, etc., to protect these liquids from contact with contaminants possibly present in the air entering these bottles to replace the volume previously occupied by the outgoing liquid. The reagent bottles and necessary supply tubing are painted black to minimize possible photochemical reagent deterioration.

Valve V_5 is necessary when air flow rates are low. This valve closes while the reagent is being injected into the system thus preventing the reagent from draining into the bottom of the contactor. The valve opens as the air pump turns on. If the reagent were to drain into the lower part of the contactor it would be impossible for the air to carry the liquid up the return tube to the top of the contactor at low air flow rates.

The cycling of the reagent with the stream of continuously sampled air continues until either (1) a pre-selected concentration of the desired pollutant is accumulated, (2) a maximum time over which the reagent remains stable in the presence of a circulating stream of unpolluted air, or (3) the reset button is manually operated. The reset time delay relay is set to control the maximum cycling time of a given charge of reagent. In the absence of the desired pollutant, the air sampling cycle will continue until this maximum time has elapsed. The time delay relay will activate the reagent change cycle and reset itself to the maximum time. Should the desired pre-selected pollution concentration be attained during a lesser time interval, the attainment of this level will activate the reagent change cycle and simultaneously reset the relay to maximum time. Similarly, pushing the reset button at any time will cause the reagent to be changed and reset the timer relay to maximum time. In the continuously recording model, an adjustable cam is mounted on each slide wire shaft of the X_1X_2 recorder which closes a micro-switch upon attainment of the pre-determined photometer output. Closing this micro-switch magnetically activates the multi-cam timer controlling the reagent change cycle as described under condition #1 above.

REAGENTS

Selection of suitable reagents for the determination of pollutants in the atmosphere in a Dosimeter type analyzer must be based on the following criteria:

1. Good sensitivity in the expected concentration range.
2. Conformity to Beer's law within the limited concentration range expected.
3. Nonsensitivity of the reagent to other ion-producing compounds frequently found in polluted atmospheres.
4. A minimum time required for the reaction to attain equilibrium.
5. Reaction stability at equilibrium.
6. A low temperature coefficient.
7. Stability of the prepared reagent.
8. A high buffering capacity with relative insensitivity of the color reaction to small changes in pH.

Hydrogen Fluoride: Study of many published analytical procedures for the fluoride ion revealed two methods conforming to most of the above ideals. The Zirconium-Eriochrome Cyanine R lake method of Megregian (18) appeared to meet all but requirement #8. It was later shown that even the reduction of HCl resulting from continued aspiration of the reagent up to 24 hours did not significantly change the color of the reagent (4).

The Aluminum-Superchrome Garnet Y method of Powell and Saylor (19) measured up to most of the requirements, but failed tests #4 and 8. Substitution of a nonvolatile buffering system for the Powell and Saylor acetic acid-acetate buffer eliminated objections to #8. The literature indicates that equilibrium is attained in 90 minutes at room temperature and in 5 minutes at 140°F. Successful application of this method might necessitate operation of the air-reagent contact system within the temperature range of 120-160°F to reduce the time required for the reagent-fluoride system to attain equilibrium. Experience in the operation of our air-reagent contactor at 120°F indicated that excessive loss of reagent through the rapid drying of spray droplets on the hot side-walls of the contactor may make the use of such elevated contactor temperatures impractical.

Initial laboratory investigation of this reagent was conducted during the first portion of the contract term (1, 2). Further study of this reagent in the automatic analyzer was discontinued because of the difficulty in obtaining a quartz flow cell. The cell has since been delivered by the vendor. Because of the other virtues of the reagent, it is believed that a limited investigation

of the reagent using the quartz flow cell would be warranted should our contract be renewed.

The Megregian reagent was modified through a 50% reduction in the concentration of hydrochloric acid used. This decrease in acidity resulted in a significant increase in the fluoride sensitivity with no noticeable change in sulfur dioxide interference, time required to attain equilibrium, color change produced by aeration loss of hydrochloric acid, etc.

A further modification of the reagent was made to retard the air oxidation of the aerated reagent. Numerous antioxidants were tried and have been reported. Technical hydroquinone, produced by Eastman Chemical Products, Inc., under the trade name Tequinol, is the most satisfactory antioxidant found to date. Further study of many other antioxidants should be made. Successful extension of this search would permit longer periods of sampling with each volume of reagent used, thus more nearly approaching the ideal situation for a dosimeter reagent.

Under conditions of the air-reagent contactor system, it would be found that rather sizeable bubbles were being produced and drawn down through the optical path. Light reflected from the surfaces of these bubbles would produce erratic photocell output. Furthermore, droplets of the reagent would hang up on the contactor walls producing an erroneous increase in light transmission of the remaining reagent. Various surface active materials were added to the reagent in an attempt to control these phenomenon. Most surface active materials produced either a bleaching of the reagent color or a reduction in the fluoride sensitivity of the reagent. Laboratory Aerosol (Fisher Scientific Company) in combination with Dow Corning Antifoam A Emulsion was found to control excessive bubble formation and reagent hang-up on the contactor walls. Addition of the silicone antifoam produced a secondary condition, which, while not completely undesirable, is tolerated because of its reproducibility. First, the glass surfaces of the contactor walls must be pre-conditioned with reagent containing the silicone anti-foam agent for a period up to 48 hours before reproducible and relatively fade-free sampling cycles are obtained on clean air. Second, the initial 15 minutes of aeration of each new volume of reagent introduced into the contactor is characterized by a 7% increase in light transmission. This initial shift is also reproducible. Both phenomenon indicate, however, that methods of improving the formulation of the reagent should be further investigated. Pre-treatment of the contactor walls with "Siliclad" might possibly eliminate the rather lengthy pre-treatment which is now required.

The light absorbance measurements are conducted with the Zirconium-Eriochrome Cyanine R reagent using the Hanovia S-4 mercury vapor light and narrow band pass optical filter peaking at 550 mu.

Reagent Preparation: Stock dye solution. Dissolve 0.7500 g. of Eriochrome Cyanine R. (National Aniline Company) in distilled

water and dilute to 1 liter.

Acidified zirconium stock solution. Dissolve 0.05655 g. zirconium hydroxide in 375 ml. of warm, concentrated hydrochloric acid (s.g. 1.19), cool and dilute to 1 liter with distilled water.

Aerosol solution, 0.05% (Laboratory Aerosol, 10% solution, Fisher Scientific Company).

Antifoam solution, 1.2% (Antifoam A Emulsion, Dow Corning Corporation).

Fluoride agent. To 500 ml. of distilled water, add 200 ml. of the acidified zirconium solution followed by 200 ml. of the dye solution. Then add 0.800 g. of Tequinol (Eastman Chemical Products, Inc.), 10 ml. of a 0.05% solution of laboratory Aerosol (10%) and 25 ml. of a 1.2% solution of Antifoam A Emulsion. Dilute to 1 liter. The prepared reagent is then transferred to a 1 liter storage bottle in the atmospheric analyzer and protected from the air with an alkaline pyrogallol trap. The reagent has been found to remain stable for periods up to 1 week.

Sulfur Dioxide: Katz (13) applied the well-known starch-iodine blue method for sulfur dioxide to the photoelectric determination of atmospheric sulfur dioxide. It was decided to utilize this reagent in the SO_2 dosimeter because of the reported stability of approximately 10^{-5}N iodine solutions during aspiration with clean air at rates of 10 liters per minute for 30 minutes or more. Our first tests indicated, however, that iodine was being volatilized from the aspirated solution. The resultant bleaching of the starch-iodine blue color was sensed by the instrument as an apparent SO_2 level in the sampled atmosphere. Preliminary studies of the Katz reagent suggested that an increase in the potassium iodide and/or starch concentration might reduce the vapor pressure of the iodine, making the reagent more stable under conditions of air aeration. Further increases in starch were found to be mechanically impossible. At the higher levels, starch deposits on the contactor walls became objectionable and removal was virtually impossible in the automatic system. The potassium iodide concentration has been increased approximately 2.7 fold with some corresponding increase in the stability of the reagent under continued aeration.

In addition it was found that a partially sulfur-dioxide-bleached blue color was more unstable under conditions of continuous aeration with clean air than was the unbleached blue color.

Many additives with varying anti-oxidant properties have been tried (3, 4) in an attempt to promote greater reagent stability under sampling conditions. A reasonably stable reagent which may be aerated at approximately 0.1 CFM for periods of 12 hours or more has been produced by the addition of small quantities of N-acetyl-p-aminophenol and mannitol. Further study of this system as well as other possible colorimetric procedures

such as the thorium borate-Amaranth dye method of Lambert, et al., (15) are indicated.

Experience gained with the starch-iodine reagent under conditions of continuous aeration in a laboratory devoid of automatic temperature controls readily revealed that the blue color of the reagent was extremely temperature sensitive. Furthermore, the color was found to deteriorate rather rapidly when stored in the dark at elevated temperatures of 120°F. To minimize these effects, the Dosimeter cabinet was thermostatted at 75°F using a refrigerative compressor to maintain this temperature.

The light absorbance measurements with the starch-iodine reagent are conducted using a 50 watt projection lamp and an optical filter peaking at 575 mμ.

Reagent Preparation: Starch solution. Dissolve 0.60 g. of soluble indicator starch in approximately 750 ml. of boiling water and cool. Select a high grade starch which will produce a typical blue color with iodine without purple tinges. Prepare freshly prior to addition of iodine solution.

Iodine stock solution, 0.01 N containing 5.6 g. of potassium iodide per liter.

Starch-iodine reagent. Add 8 ml. of the iodine stock solution to the cooled starch solution. To this solution add 3.0 g. of monobasic sodium phosphate, 12.0 g. of mannitol and 0.090 g. of N-acetyl-p-aminophenol. Dilute to nearly 1 liter and adjust the pH to 6.0 with the sodium hydroxide solution using a pH meter. Transfer to a 1 liter volumetric flask and dilute to the mark. The prepared reagent is then transferred to a 1 liter, black reagent storage bottle in the automatic analyzer. A drop of mercury is kept in the storage bottle to act as a fungicide. Clean, sterile containers should be used. The reagent has been found to remain stable up to 1 week when handled in this manner. A soda lime-activated charcoal trap on the reagent bottle air inlet protects the reagent from possible contamination from air pollutants.

PERFORMANCE

Hydrogen Fluoride: Figure 7 A indicates the response of the reagent and instrument to a 4 ppb (parts per billion) HF atmosphere developed in a small laboratory gas chamber. Figure 7 B shows a record of a similar reagent cycle obtained while sampling an atmosphere containing 0.5 ppm sulfur dioxide for 4 hours. Figure 7 C shows a typical curve obtained while sampling air which had passed through a soda-lime-activated charcoal tower. The response of the reagent to other major pollutants which has been identified in the atmospheres of various urban areas has not yet been established. A study of the effect of a number of these pollutants should be undertaken.

Sufficient time was not available to make a study of the

absorption efficiency of the gas contactor system utilized in the analyzer. A relatively high efficiency has been assumed, since the calculated analyzer concentration of 4.0 ppb HF of Figure 7 A compared quite favorably with the chemically determined concentration of 4.1 ppb HF. Similar comparison runs should be conducted at higher and lower fluoride levels to assess completely the absorption efficiency of the contactor.

It is common knowledge that a large proportion of the effluent from aluminum reduction plants consists of a fume closely approximating cryolite. Because this fume is sub-micron in size and because of the relatively high acidity of the fluoride reagent, it is possible that these fluoride-containing particulates might react to some degree with the reagent. The collection and reaction efficiency of such particulates in the contactor should be studied under controlled laboratory conditions. This represents an important facet in the problem of sampling and reporting concentrations of atmospheric fluorides. Since the effects of gaseous and particulate fluorides on plant life are thought to be appreciably different, a method of differentiating between the two forms of fluorides is required. No attempt was made to effect a separation before passing the sampled air through the contactor in our field sampling tests. Filtration was not attempted since no information is available concerning adsorption, absorption and reaction losses of gaseous fluorides on the filter media. This would indicate that studies involving the separation of gaseous and particulate fluorides should also be conducted.

Figure 8 shows several typical records of the optical measurements obtained during field operation. Figure 8 A shows the reagent response obtained in the field near Mead, Washington under conditions of south wind with no known source of fluoride up-wind. Figure 8 B was obtained under similar conditions of south wind at Waneta, British Columbia, located at the Canadian border on the Columbia River. Figure 8 C and 8 D exemplify two conditions under which fluoride fumigations were experienced near Mead. Figure 8 C was obtained during a period of variable winds in which some northerly wind flow across a large aluminum reduction plant was recorded. Figure 8 D illustrates the record obtained during the early morning break-up of a typical summer inversion layer at the Mead sampling site.

Figure 9 is a calibration curve based on added sodium fluoride which was used to determine the concentration of fluoride which had been accumulated by the circulating volume of reagent. Atmospheric concentrations of fluoride in terms of parts per billion hydrogen fluoride may be caluclated for any desired time span during a given reagent cycle by dividing the micrograms of fluoride found by the corrected cubic meters of air sampled during the selection time span. In practice, Figure 9 would be reproduced on a clear plastic sheet and placed over the record of each cycle to facilitate the transcription and calculation of the data. Once the absorption efficiency studies have been completed, this overlay should be re-drawn to correct for any error introduced through the assumption of 100% absorption

efficiency.

The continuous record may be read within an instrument and reagent error of approximately ± 1%T which is equivalent to 2 micrograms of fluoride under the conditions of instrumental analysis. The error of the maximum average concentration of fluoride in the atmosphere within a maximum sampling cycle of 4 hours would be in the order of ± 6%. This error, of course, would increase as the amount of fluoride collected within a given 4 hour period decreased from the maximum determinable of 30 micrograms to a minimum detectable in the order of 1-2 micrograms. In the latter case the percentage error introduced would be in the order of ± 50%. This is equivalent, however, to an actual error of approximately ± 0.16 ppb hydrogen fluoride.

Obviously the sensitivity of the instrument could be increased proportionately to any increase obtainable in the contact rate between sampled air and circulating reagent assuming no corresponding decrease in absorption efficiency. A study of methods of increasing the air sampling rate should be undertaken with a view toward increasing the sensitivity of the analyzer.

Inspection of the typical curves shown in Figure 8 shows frequent instantaneous "pips" extending to the right of the curve. These irregularities, related to the activation of the water level injection mechanism, developed when the recorder, colorimeter and liquid level control circuitry were mounted within the metal cabinet. Prior to this stage of instrument development, no interaction between the liquid level control system and the recorder had been noted. Thus far, it has not been possible to eliminate this phenomenon from the continuous record. Curiously, however, this interaction does not exist in the sulfur dioxide system mounted within the same metal cabinet.

Sulfur Dioxide. Figure 10 A indicates the response of the reagent to air having previously been passed through a soda lime-activated charcoal tower. Figure 10 B shows a typical reaction curve obtained while sampling an atmosphere containing 0.5 ppm sulfur dioxide at a rate of 0.08 CFM. Figure 10 C and 10 D were obtained in the field near Mead, Washington. Figure 10 C was obtained under conditions of south wind with no major source of sulfur dioxide upwind. Figure 10 D was obtained during the early morning break-up of a typical summer inversion.

ACHIEVEMENTS

During the 15 month term of the present contract, the following have been accomplished:

I. Instrumentation

A. Two similar automatically controlled, versatile dosimeter systems have been developed which will

(a) scrub a continuously sampled air stream through a small volume of continuously circulating reagent, concentrating the desired pollutant therein; (b) maintain the initial volume of the reagent through replacement of evaporation losses by the intermittant addition of small increments of make-up water; (c) utilize reagents which are reasonably specific for a variety of atmospheric pollutants; (d) sense the optical character of the reagent continuously, thus measuring the pollutant accumulated therein; (e) actuate a time stamp printer to record the optical character of the circulating reagent; (f) discharge the spent reagent upon either attainment of the preselected dose concentration therein, or upon completion of some pre-selected maximum time during which the reagent is permitted to cycle; (g) introduce a new, measured volume of reagent into the air-reagent contactor system; and (h) control the continuous and automatic cycling of the Dosimeter within the limits outlined above.

B. A basically versatile instrument design has been developed which permits potential application of the instrument to the sampling, analysis and recording of levels of atmospheric pollutants for which colorimetric methods are available or can be devised. Conditions which may be varied to attain this versatility include (a) air sampling rate, (b) reagent, (c) light wave band from short ultra violet through the visible range, (d) reagent flow rate, (e) temperature of the air-reagent contactor system, and (f) optical system to permit either colorimetry in the visible light range or fluoroimetry. Any of these changes may be easily made without disturbing the basic instrument.

II. Reagents

A. Hydrogen fluoride. A reagent which meets all of the requirements for Dosimeter application with the exception of long term stability under conditions of continuous aeration has been developed. Utilization of the Zirconium-Eriochrome Cyanine R reagent is limited to aeration periods of 4 hours. Selection of the dosimeter accumulation of fluoride at sufficiently low concentrations permits dosimeter application of this reagent within 4 hours maximum reagent cycles. The reagent has been successfully used in the continuous recording model of the analyzer. This combination of instrument and reagent may prove to be the first successful automatic atmospheric fluoride analyzer. (Since completion of the contract period a new fluoride reagent formulation has been developed which permits upwards to 24 hour cycles).

B. Sulfur dioxide. A reasonably satisfactory reagent for sulfur dioxide has been developed. The reagent provides greater sulfur dioxide sensitivity than is possible with the Thomas Autometer or the Titrilog. Selection of the dosimeter level within low concentration limits permits dosimeter application of this reagent within 12 hour maximum reagent cycles.

III. Field Testing.

The two versatile Dosimeters with continuous recording features, one utilizing the starch-iodine blue reagent and the other with the Zirconium-Eriochrome Cyanine R reagent, were mounted in the Division of Industrial Research Air Pollution Section's 35' mobile air pollution laboratory, Figure 11. Sulfur dioxide levels were simultaneously recorded on the Leeds and Northrup Thomas Autometer, the Consolidated Electrodynamic Corporation Titrilog and the new Dosimeter. Hydrogen fluoride levels were recorded on the new Dosimeter and compared with the results of the chemical analysis of alkaline scrubbing solutions corresponding to each fluoride Dosimeter sampling cycle. The average fluoride levels for the entire sampling period at each sampling site were compared with the fluoride levels accumulated in limed filters exposed at each sampling site during the sampling period. Wind speed and direction data was recorded, as was the "sootiness" of the air on a moving filter tape.

PROBLEMS REQUIRING FURTHER INVESTIGATION

I. Reagents

A. Zirconium-Eriochrome Cyanine R for fluorides.

1. Develop better formulation capable of longer periods of aeration thus improving the value of the reagent for use in Dosimeter. Included would be a search for better antioxidants, antifoamers, etc.

2. Develop quicker methods for or eliminate necessity for "pretreatment" of the glass contactor walls. This procedure is presently required to prevent an apparent bleaching of the reagent color under conditions of aeration with clean air.

B. Aluminum-Superchrome Garnet Y for fluorides.

Investigate suitability of this reagent for Dosimeter application using the non-volatile buffer system previously developed (1, 2). This would include establishing the stability

of the reagent under continued aeration, time required to attainment of equilibrium, etc.

C. Starch-Iodine blue for sulfur dioxide.

1. Continue studies to determine the optimum starch-iodine ratio compatible with prevention of starch deposits on contactor walls and volatilization losses of iodine under continuous aeration.

2. Continue study of influence of reagent additives such as antioxidants, surface active materials, etc. to improve reagent stability for Dosimeter application under conditions of continuous aeration.

D. Thorium Borate-Amaranth dye reagent.

Investigate possible dosimeter application of this procedure.

II. Absorption Efficiency Studies.

Following development of improved reagents for sulfur dioxide and hydrogen fluoride, determine the absorption efficiencies obtained in the contactor system under the air flow rates required sensitivity, expected atmospheric concentrations and physical flow rate limitations of the contactor system.

III. Interfering Ions

A. Determine the influence of major known pollutants upon the response of the hydrogen fluoride and sulfur dioxide reagents. Establish tolerable limits.

B. With particular reference to the fluoride reagent, determine reagent response to submicron cryolite fume.

IV. Separation of Gaseous and Particulate Fluorides.

If the studies proposed in III-B above indicate a significant response of the fluoride reagent to particulate fluorides, methods of separating gaseous from particulate fluorides should be investigated. Practical application of successful methods might result in a two step sampling cycle in which (1) total fluorides and (2) either gaseous or particulate fluorides would be determined separately and then the unanalyzed type calculated by difference.

V. Contactor Studies.

A method of increasing the air flow rate through the gas contactor system which will not produce an equivalent reduction in absorption efficiency is needed to increase the potential sensitivity of the Dosimeter. Such a development would increase the applicability of the instrument to the study of fluorides, odors and other pollutants present in the atmosphere in the parts per billion range. Redesign of the present system or substitution of a new contactor system such as a small venturi scrubber might permit greater potential sensitivity.

VI. Design Simplification and Improvement.

A. Simplification of construction and cost reduction could be achieved in the reagent injection system. A timer cam controlled solenoid valve placed in the reagent line between the storage bottle and the contactor could be substituted for the present complicated system consisting of a motor-driven syringe pump, check valves and reagent input line valve.

B. It is believed that some improvement in colorimeter design could be attained through design of a system built specifically for the Dosimeter. A system of balanced photocells might make it possible to reduce the frequency of manual colorimeter balancing which is required for the 501-M. It also appears that this might result in concurrent reduction in the cost of that component.

VII. Further Field Testing.

Following the incorporation of design and reagent improvements into the Dosimeter, further field testing should be conducted to establish the practicability of the system. The Dosimeter should be taken into several additional areas within the Pacific Northwest to obtain operational data. At least six to eight weeks field sampling during the summer of 1958 should be attempted. Possible sampling sites would include; Tacoma, Longview, Wenatchee, Kellogg, etc.

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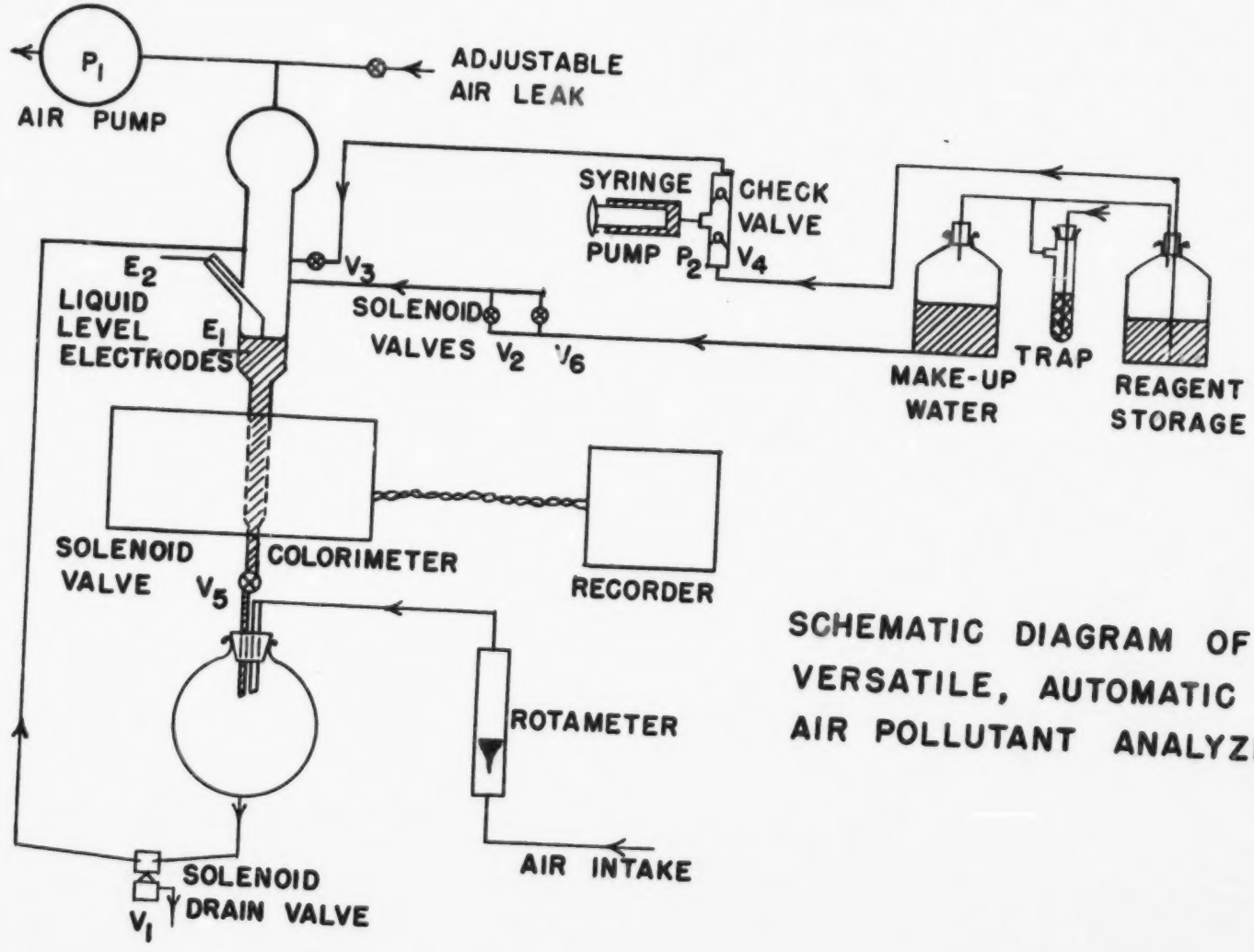


SCHEMATIC DIAGRAM OF VERSATILE, AUTOMATIC AIR POLLUTANT ANALYZER

FIGURE 1

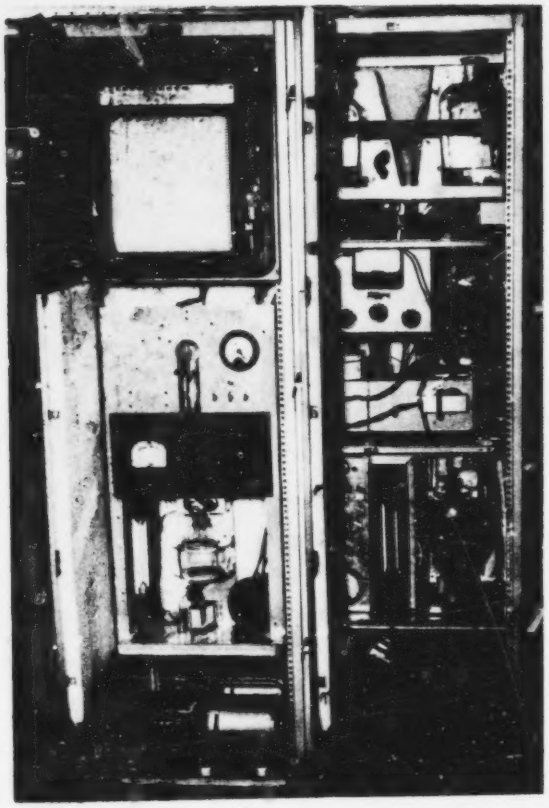


Figure 2

Interior Views
"Universal" Air
Pollutant Analyzer

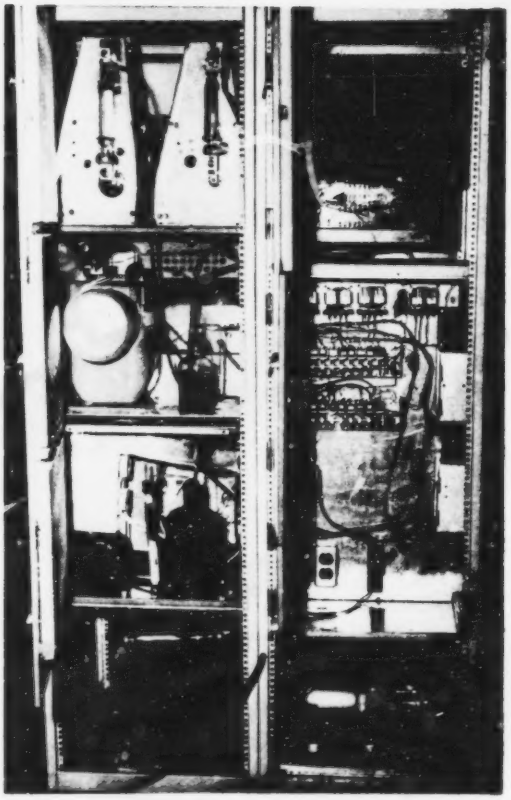
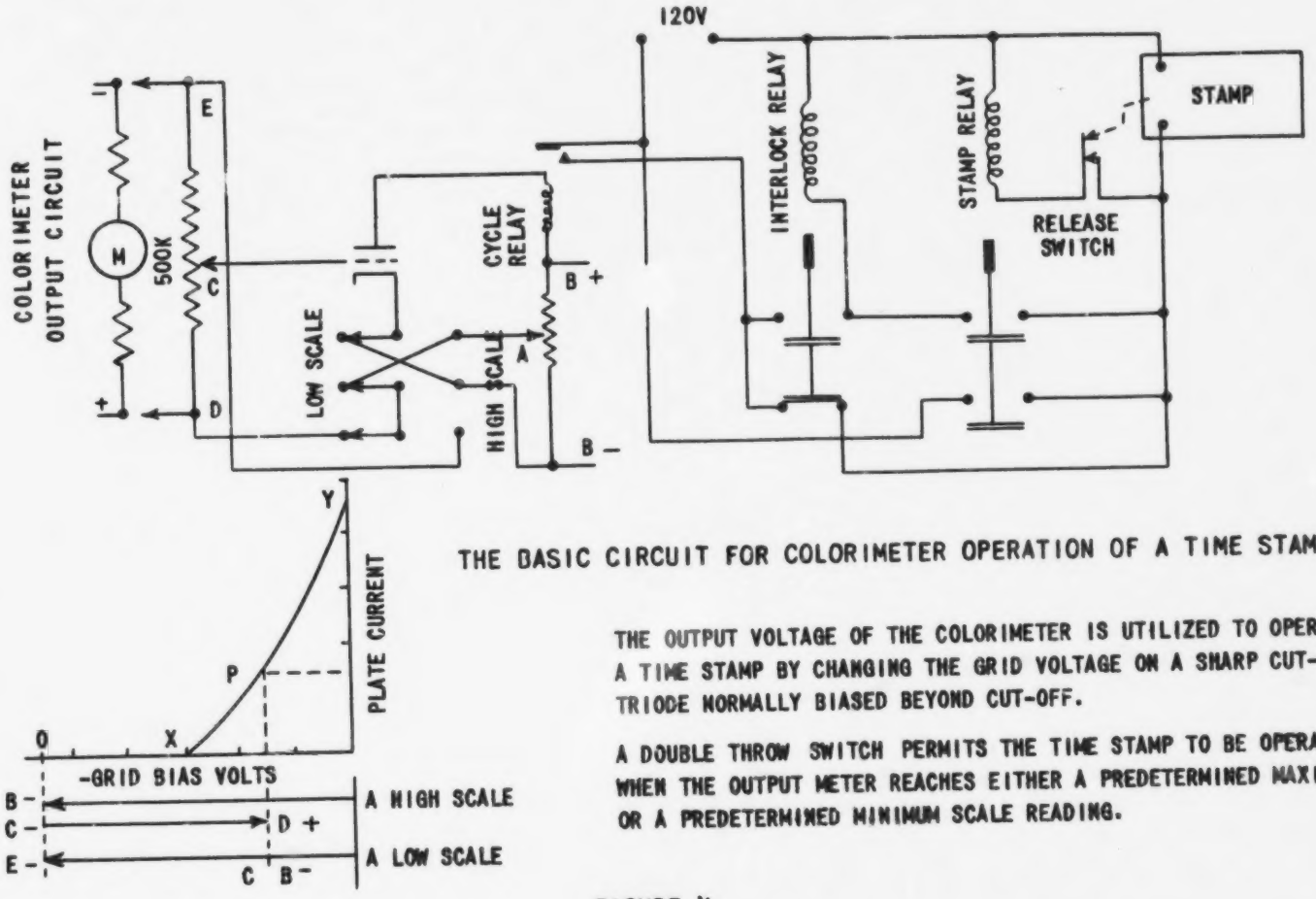


Figure 3



THE BASIC CIRCUIT FOR COLORIMETER OPERATION OF A TIME STAMP

THE OUTPUT VOLTAGE OF THE COLORIMETER IS UTILIZED TO OPERATE A TIME STAMP BY CHANGING THE GRID VOLTAGE ON A SHARP CUT-OFF TRIODE NORMALLY BIASED BEYOND CUT-OFF.

A DOUBLE THROW SWITCH PERMITS THE TIME STAMP TO BE OPERATED WHEN THE OUTPUT METER REACHES EITHER A PREDETERMINED MAXIMUM OR A PREDETERMINED MINIMUM SCALE READING.

FIGURE 4

AIR-REAGENT CONTACTOR DETAIL

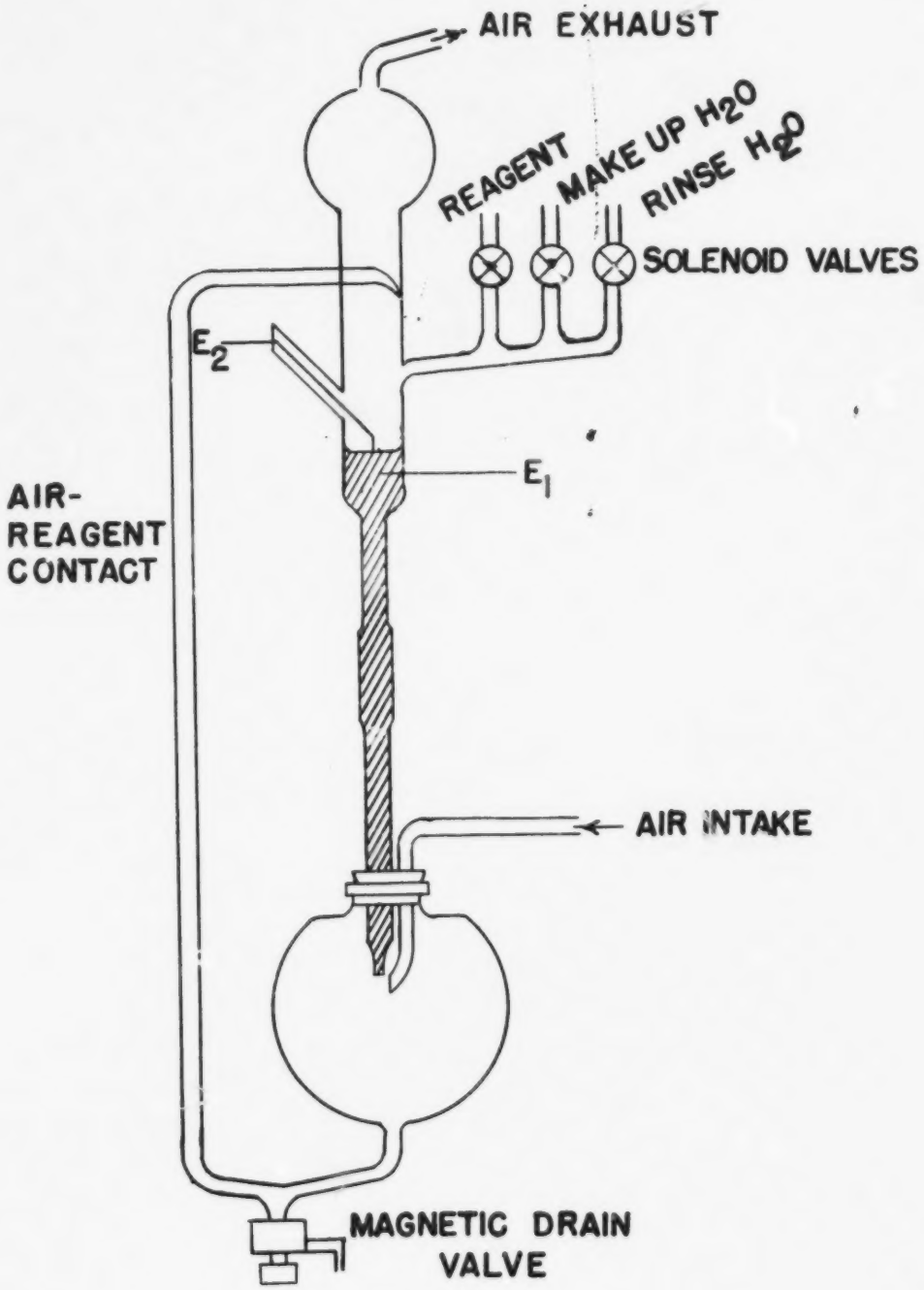
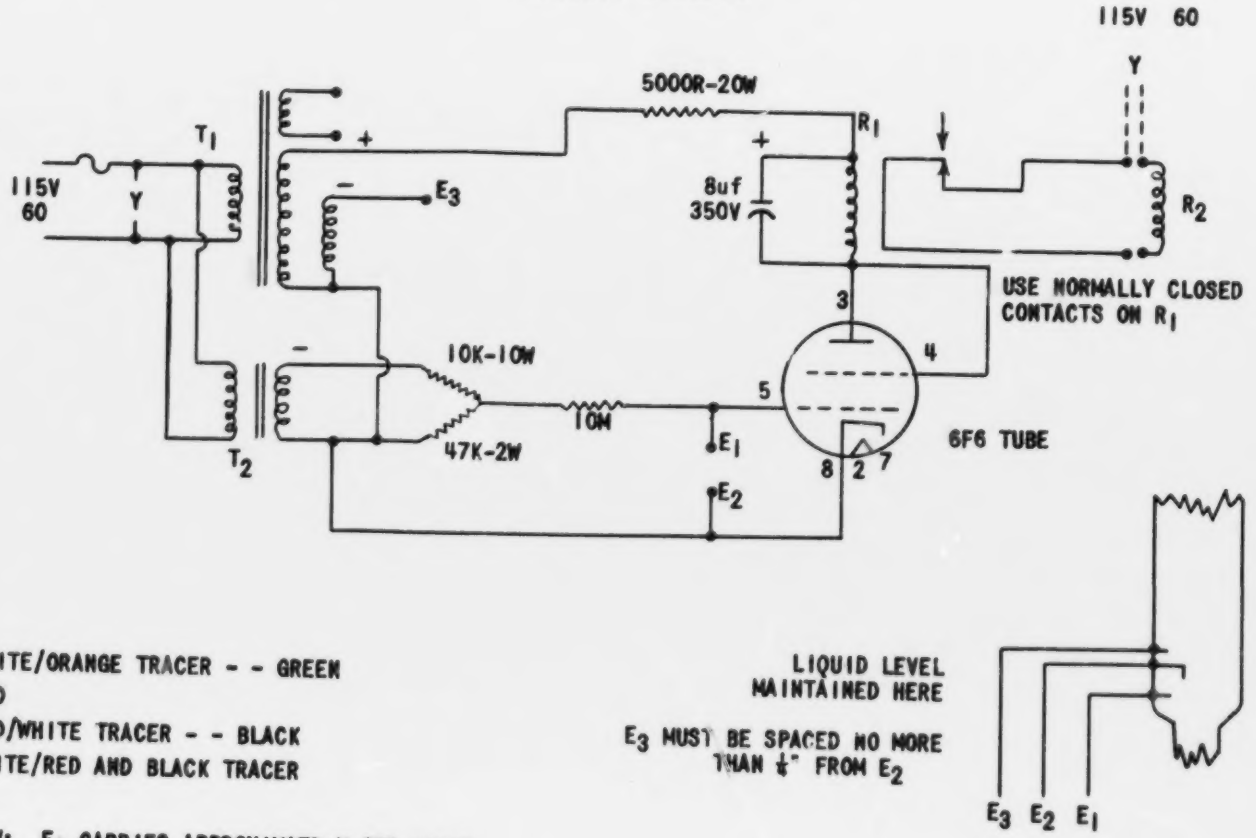


FIGURE 5

LIQUID LEVEL CONTROL SYSTEM
CIRCUIT DIAGRAM



E_1 WHITE/ORANGE TRACER - - GREEN
E_2 RED
E_3 RED/WHITE TRACER - - BLACK
R_2 WHITE/RED AND BLACK TRACER

CAUTION: E_3 CARRIES APPROXIMATELY 375 VOLTS

FIGURE 6

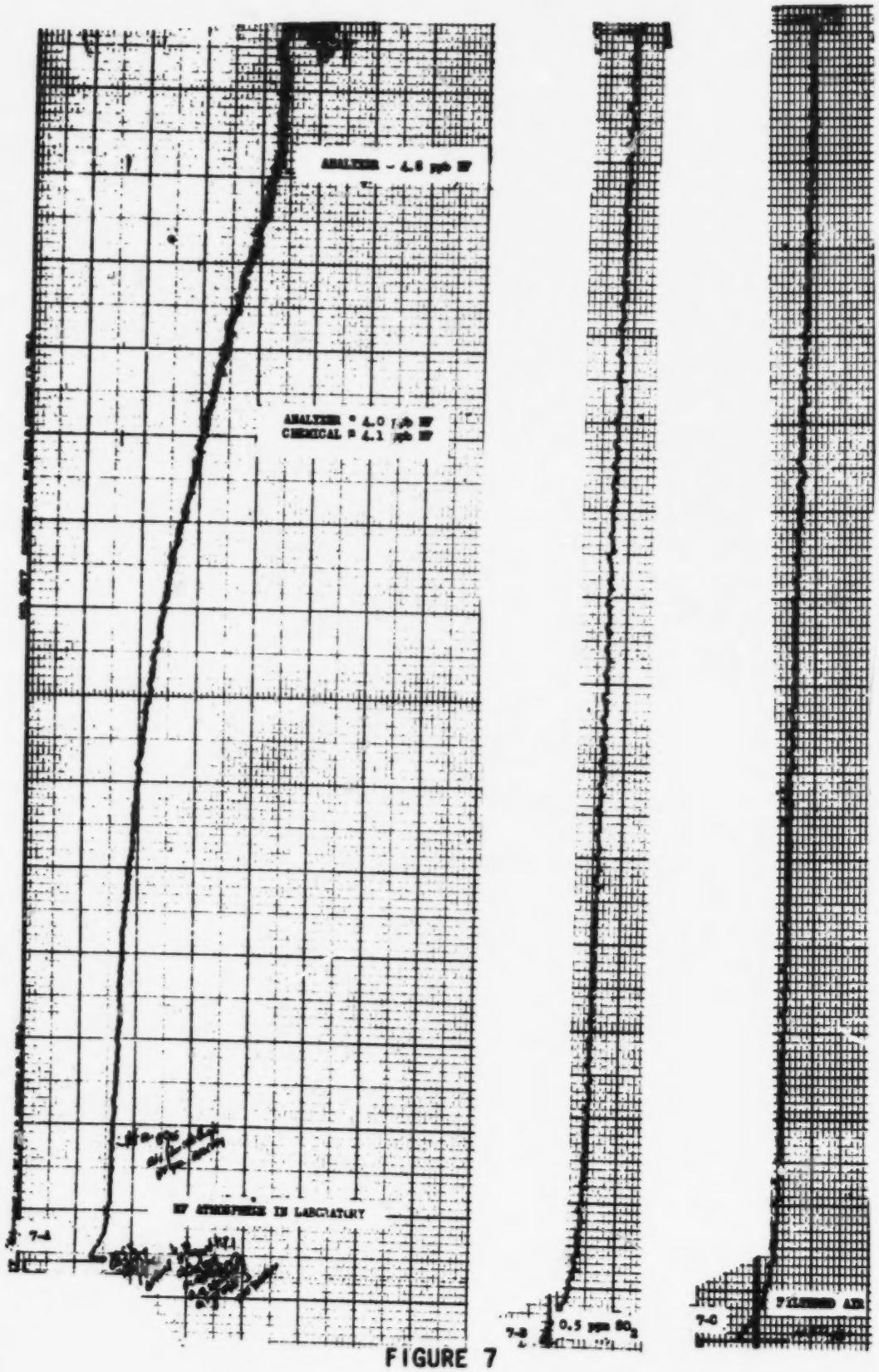

ANALYZER - 4.0 ppb
ANALYZER = 4.0 ppb
CHEMICAL = 4.1 ppb
AIR ATMOSPHERE IN LABORATORY
7-4
0.5 ppm SO_2
7-0

FIGURE 7

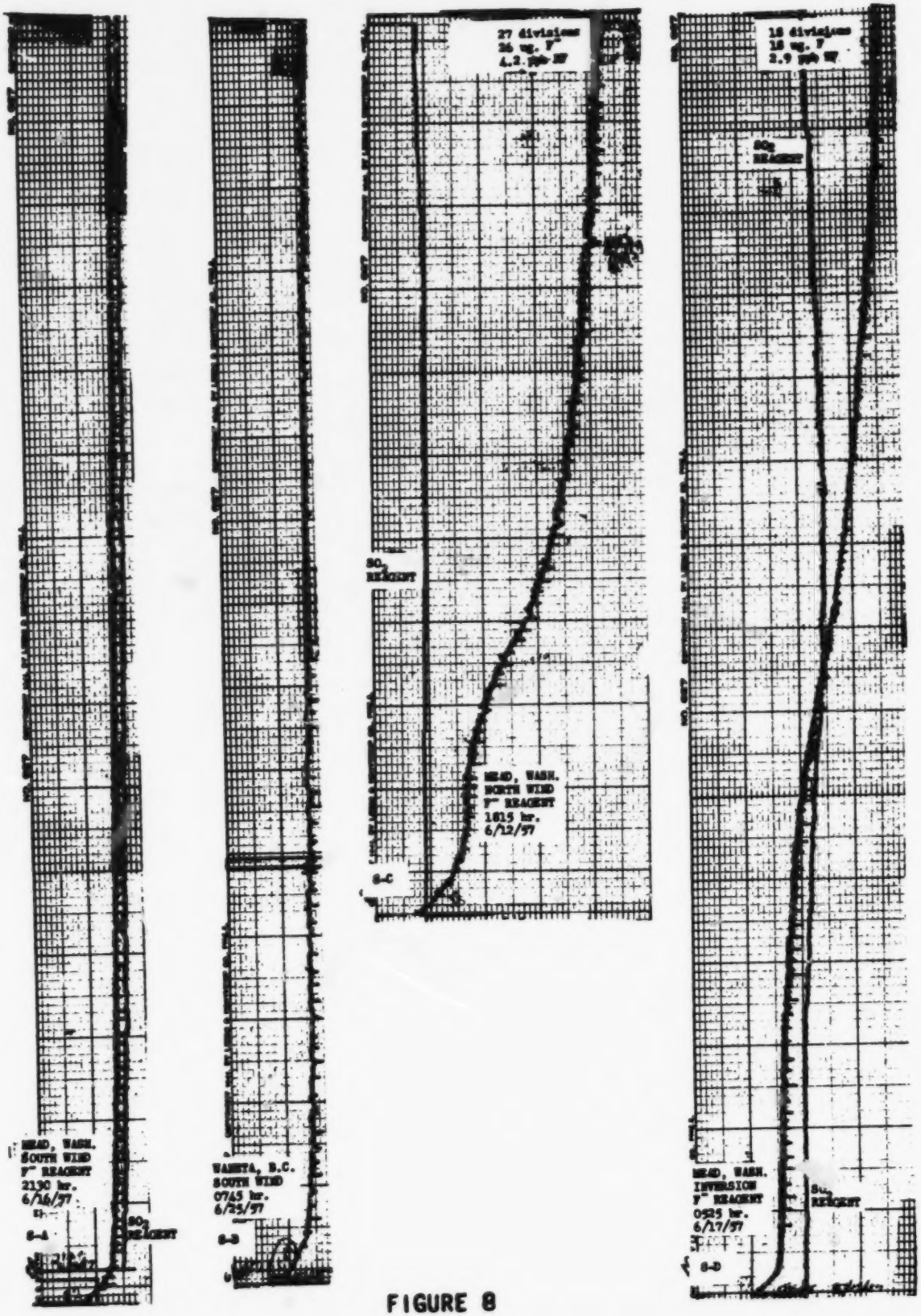

HEAD, WASH.
SOUTH WIND
F° REACHENT
2130 hr.
6/16/57
WAHETA, B.C.
SOUTH WIND
0745 hr.
6/25/57
HEAD, WASH.
NORTH WIND
F° REACHENT
1815 hr.
6/12/57
HEAD, WASH.
INVERSION
F° REACHENT
0525 hr.
6/27/57

FIGURE 8

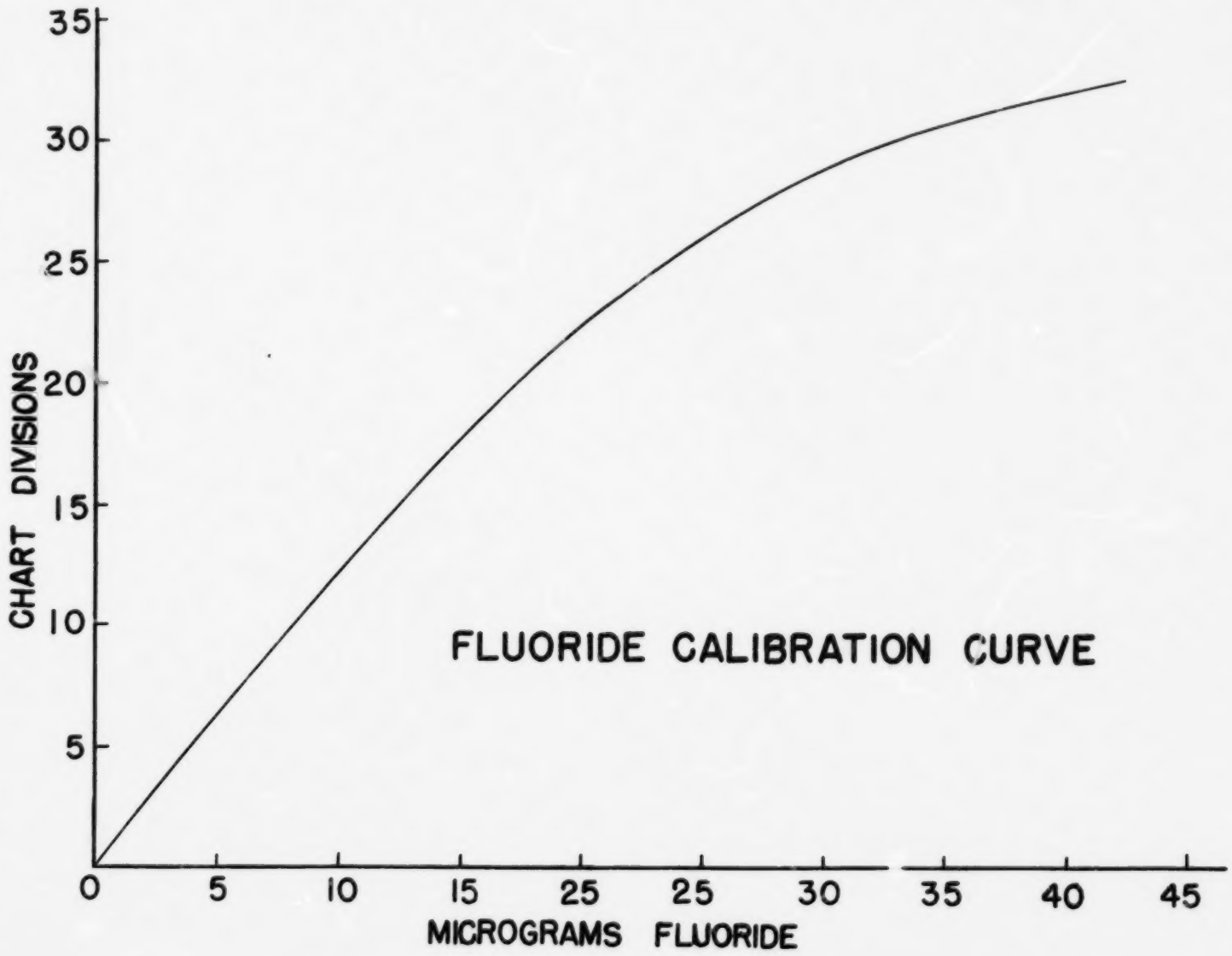
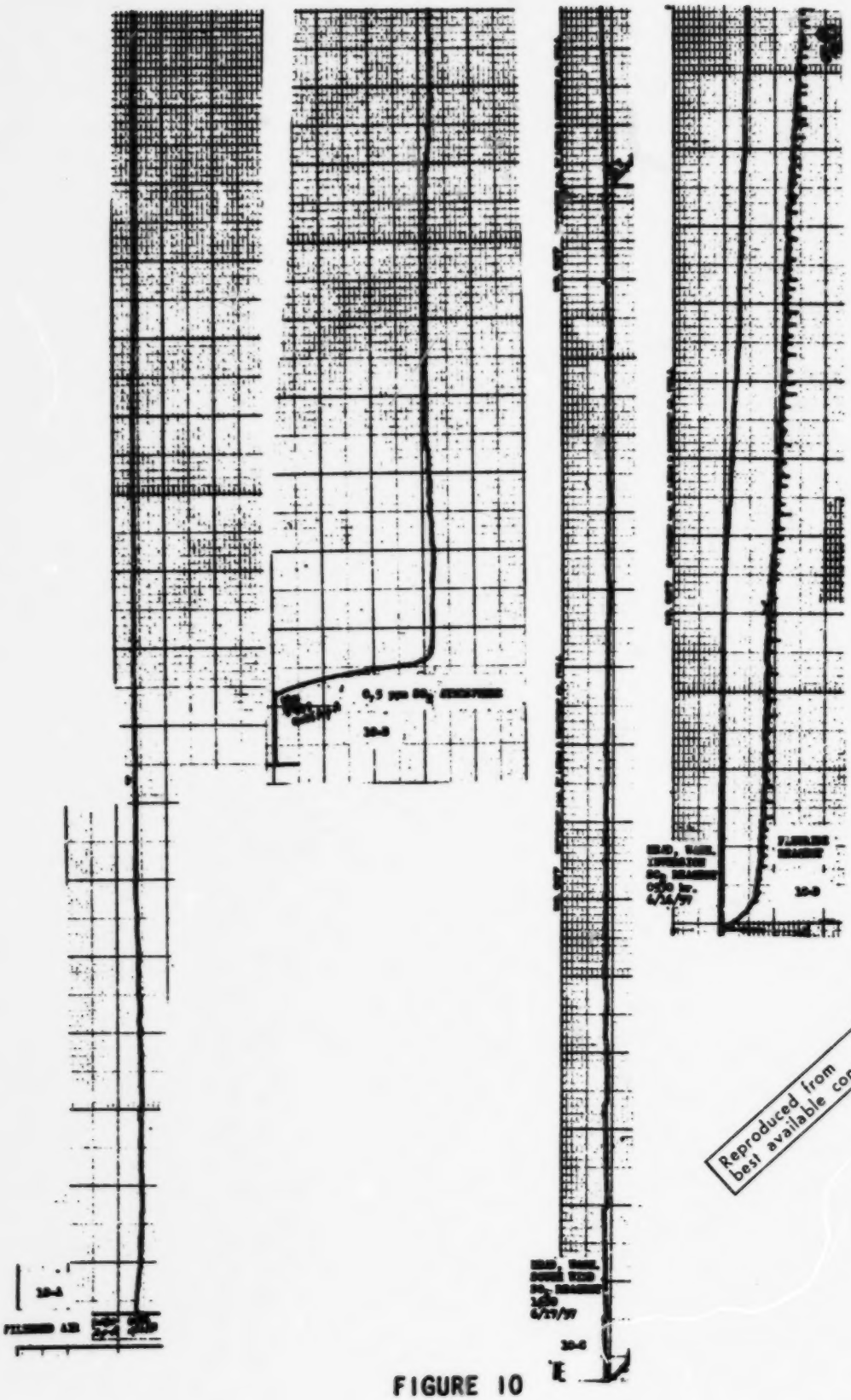

35
30
25
20
15
10
5
CHART DIVISIONS
FLUORIDE CALIBRATION CURVE
0
5
10
15
25
25
30
35
40
45
MICROGRAMS FLUORIDE

FIGURE 9



Reproduced from best available copy.

FIGURE 10

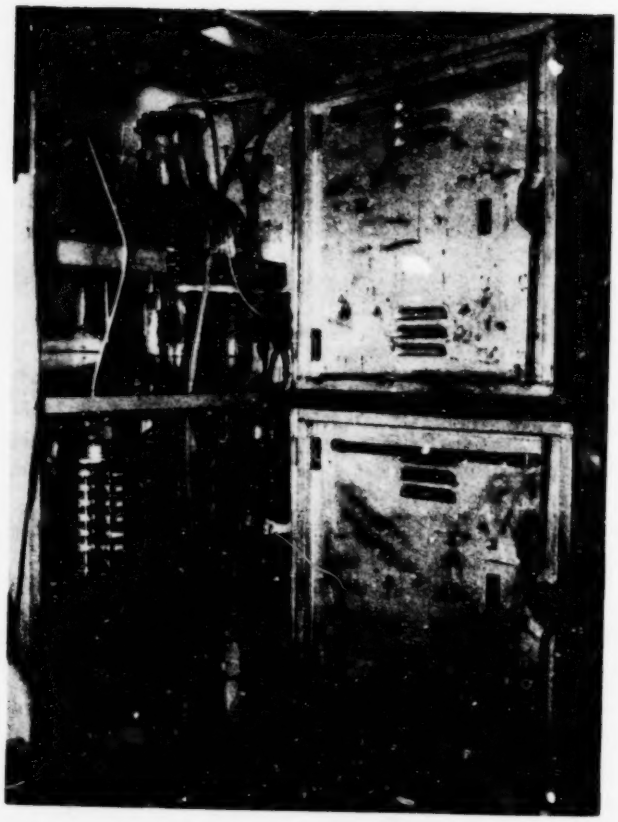
Figure 11

Exterior Views of Mobile Air Pollution Laboratory on Location at Waneta British Columbia on the Columbia River.

Office Area

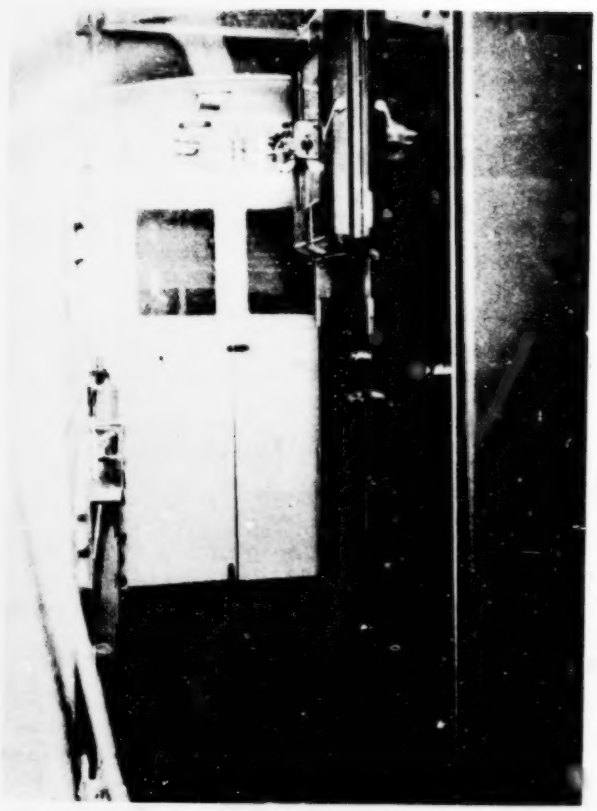
Figure 12 Mobile Air Pollution Laboratory

Titration Area



Automatic Scrubbing Sample Collector

Figure 13



Exterior View of HF-SO_2 Analyzer in Mobile Laboratory

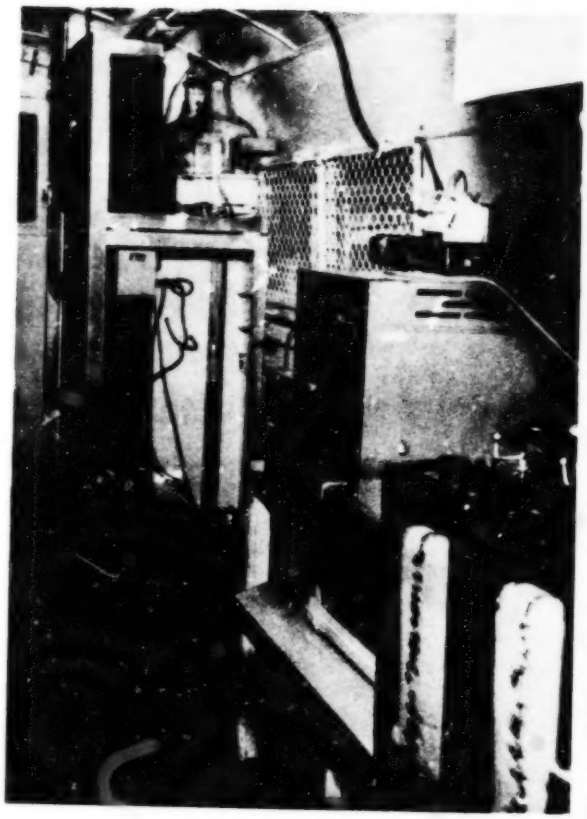
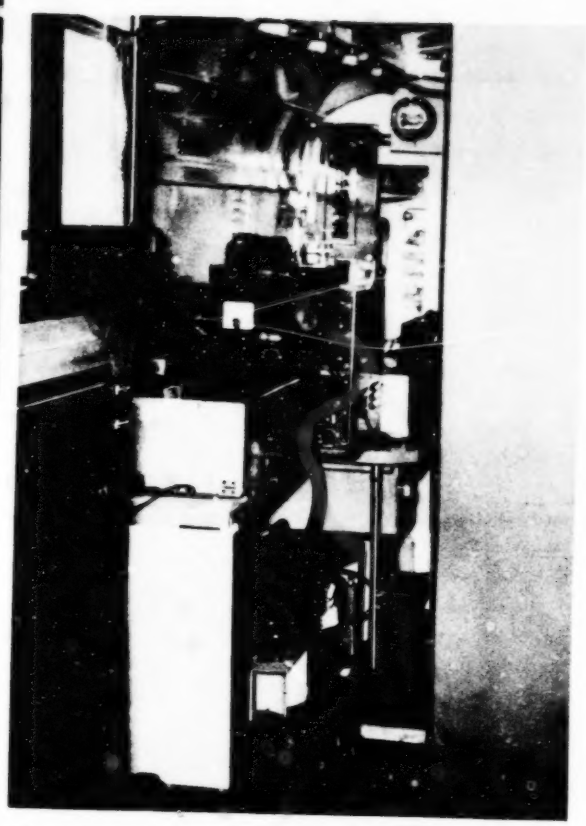


Figure 14



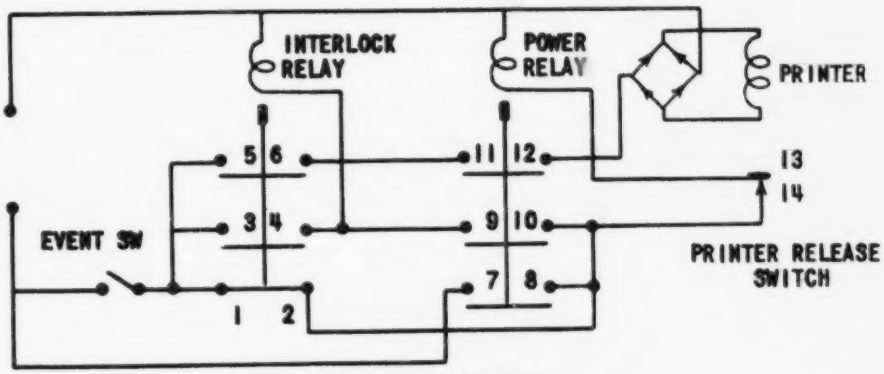
Left Side Views of Mobile Air Pollution Survey Laboratory Showing Thomas SO_2 Analyzer, Atmospheric Radiation Recorder, B-W Climate Survey and HF-SO_2 Analyzer Cabinet.

AIR POLLUTION RECORDER
POWER BUS

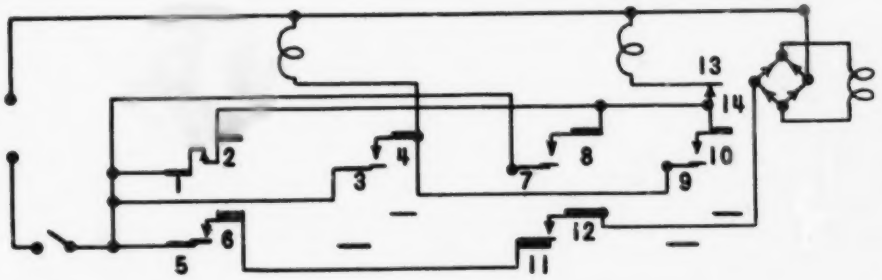
(1) RIGHT AND LEFT WHEN FACING FRONT OF CABINET

PRINTER CONTROL CIRCUIT

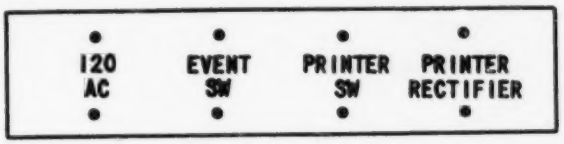
A PROLONGED CLOSING OF THE EVENT SWITCH PROVIDES ONLY AN INSTANTANEOUS PULSE TO THE PRINTER



CIRCUIT DIAGRAM

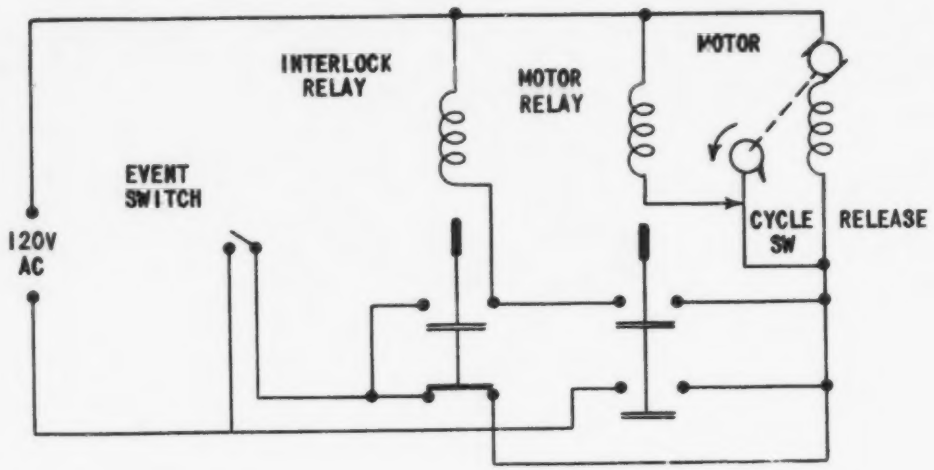


CONNECTIONS TO SWITCH BLADES ON RELAYS



TERMINAL BOARD

AIR POLLUTION RECORDER

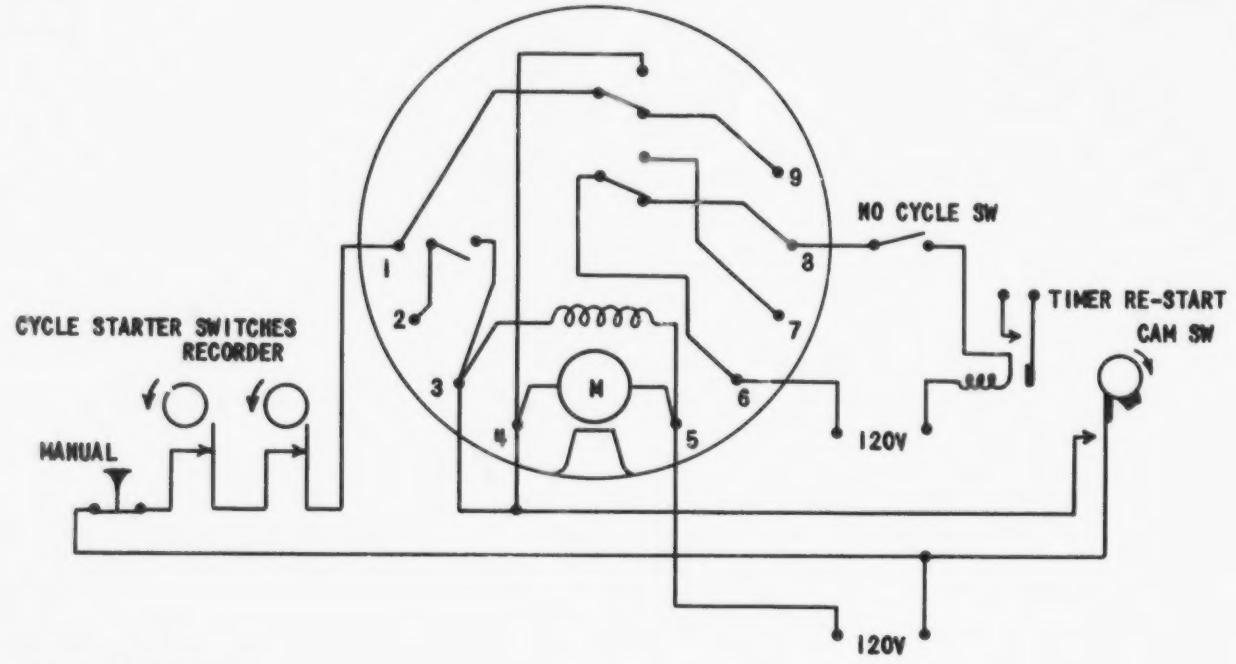


CYCLE SWITCH

FOR AIR POLLUTION LIQUID SAMPLING PUMP

1. CLOSE EVENT SWITCH WHICH STARTS MOTOR AND CLOSES SELF-LOCKING MOTOR RELAY WHICH IN TURN CLOSES INTERLOCK RELAY.
2. WHEN MOTOR HAS COMPLETED ITS CYCLE IT TURNS ITSELF OFF BY OPENING MOTOR RELAY.
3. IF EVENT SWITCH IS STILL CLOSED, IT HOLDS THE INTERLOCK CLOSED, WHICH PREVENTS MOTOR FROM BEING STARTED AGAIN UNTIL THE EVENT SWITCH IS OPENED TO RELEASE INTERLOCK RELAY.

CRAMER TIMER SWITCH



AIR POLLUTION RECORDER

AUTOMATIC CYCLING SWITCH
STARTS A CYCLE BY:

1. ELAPSED TIME INTERVAL
2. HIGH (OR LOW) LIMIT SWITCH ON RECORDER
3. MANUAL SWITCH